Production of Propionic Acid from Syngas

Team Echo:

Sabah Basrawi

Alex Guerrero

Mrunal Patel

Kevin Thompson

Client Mentor: Shannon Brown

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28. **EXECUTIVE SUMMARY**
    1. Abstract

With an estimated world production of capacity of 377,000 metric tons in 2006, propionic acid is an important organic acid that does not receive much publicity. Propionic acid – which occurs naturally in apples, strawberries, grains, cheese, and human sweat – is mainly used as a mold inhibitor for various animal feed and baked goods as well as a preservative in cheeses. It is also a significant precursor in many industrial processes such as pharmaceuticals, plastics, plasticizers, textile and rubber auxiliaries, dye intermediates, as well as flavorings and cosmetics. The plant designed for this project has a projected production rate of 16,000 tons of propionic acid per year. The initial feedstock will comprise of sygnas (a mixture of CO and H­2) and ethylene, which will react in a process known as carbonylation in the presence of a rhodium based catalyst to produce propionaldehyde and ethane. The ethane will be removed from the system and sold back to Lyondellbasell (from where the ethylene is acquired) and the propionaldehyde will then be oxidized to produce propionic acid. The market demand for propionic acid is expected to grow at around 2.3% per year regardless of the state of the economy since food production and preservation are highly dependent upon it.

The location of this plant, as well as the plant being designed by team foxtrot, will be located in Morris, Il 60450 in order to be closer to Lyondellbasell. The reason to be close to Lyondellbasell is because of the difficulty in transporting ethylene is much greater than that of coal. The inconvenience experienced by team foxtrot by being a few hours away from their coal source is minimal in comparison with the distress that would have been found by team echo with ethylene transport.

Based upon the economics of the process it is the recommendation of the process engineers that the process not be completed. With a capital cost of 57.8 million dollars, yearly expenses of around $28 million and yearly profit of around $ 29 million, it would take 18.5 years for the project to break even. Thus the IRR and NPV values show that the process would be a non-profitable venture.

1. **DISCUSSION** 
   1. **Process Overview**

The production of propionic acid was chosen due to the amount of industrial applications. While the food industry will be a main target of Team Echo, other avenues will also be explored (see Appendix XI).

* + 1. Production of Propionaldehyde

Ethylene will be obtained at 450 psi pressure and 70 ° F temperature. Syngas will be obtained at the prescribed temperature and pressure of 290 psia and 212 ° F. Ethylene will be heated to 212 ° F which is the reaction temperature. Both ethylene and syngas will be fed into the reactor at the reaction specifications in order to produce propionaldehyde and ethane as a side product. Propionaldehyde is a precursor to propionic acid, and is the aldehyde for of propionic acid. The conversion of the reactants to the aldehyde is not one hundred percent and thus there will be unreacted reactants in the product stream. The amount of by-products produced was higher than originally anticipated with a 50% selectivity towards the ethane by-product. Because of this the 33,000 ton per year goal will not be met due to a need for more hydrogen in the system. 16,000 tons/year will be produced thus halving the profit of this process. In order to purify the Propionaldehyde from the ethane, the product will be distilled in order to remove some of the Propionaldehyde. Once this has been done the product will be sent into an absorbing column in which butane will be used to absorb the ethane from the major intermediate product. The ethane and butane will be sent into a stripping column in order to be separated from one another. The unreacted reactants, which also come from the absorber, will be also be separated from butane in another stripping column. The reason for the recovery of butane is that it needs to be reused. The purified propanal streams will be sent on to the second reaction process which will oxidize the aldehyde to its carboxylic acid form of propionic acid.

A heat exchange reactor will be used to carry out the aldehyde synthesis reaction and will be purchased from Chart Energy & Chemicals, Inc. It will be made of stainless steel, which is more expensive that carbon steel, but the corrosive properties of propionaldehyde are unable to be supported by carbon steel. The reaction will be catalyzed using a rhodium catalyst which will be immobilized in the reactor. Because of this, separation of the catalyst is not a problem and because rhodium has a very long catalyst life, it will not have to be bought often.

* + 1. Oxidation of Propionaldehyde

The propionaldehyde product from the first reaction is heated to the proper reaction conditions temp 122° F and pressure 14.7 psia. Oxygen is used to oxidize the aldehyde into its carboxylic acid form. Oxygen is brought in as air and through a membrane separation; a gaseous mixture of 85% oxygen at ambient conditions is acquired and heated to the proper temperature using a feed-effluent heat exchanger. Propionic acid is produced in this reaction, with unreacted reactants and catalyst also flows from the reactor. To catalyze the oxidation reaction, a cobalt halide is dissolved in water and the cobalt ion acts as the catalyst. The water component of this mixture is miscible with the propionic acid final product which is an issue that is dealt with during the purification part of the process. The cobalt halide is precipitated by concentrating the solution and separating in series until the final product has been appropriately purified. The mass purity of the final product is slightly lower than the industrial standard at a purity of 99.3%.

1. **CONCLUSIONS AND RECOMMENDATIONS**

The reason for choosing to produce Propionic acid was because of its wide range of uses, with a focus on the food preservative aspects of the product. It was the assumption of the group that there would always be a market for propionic acid as there is always a demand for food regardless of the state of the economy, and in times of economic boom there will be a greater market for the other uses of Propionic acid.

A project goal of 33,000 ton/year was selected after learning that the largest producer of Propionic acid, BASF, produces 88,000 ton/year. As BASF is a majority of the market at approximately 40% team echo felt it would be reasonable to target approximately 10% of the market as a new company with room for expansion. Had the goal of 33,000 tons/year been met then the process would have been a profitable one which could have been a viable option. As the need for more hydrogen was realized late in the progression of the project it was not possible for team foxtrot to increase the hydrogen content of their syngas. More ethylene from Lyondellbasell is also needed in order for the process to move forward. Due to the economics now that the process is running at half production team echo must recommend that the process not be completed as it is. The break even point for the process occurs at 18.5 years and that coupled with a negative net present value indicates that the process not move forward without more hydrogen to have the process run at full production.

**APPENDICES**

1. **Design Basis**
   1. Commercial Production

Propionic acid – which occurs naturally in apples, strawberries, grains, cheese, and human sweat – is mainly used as a mold inhibitor for various animal feed and baked goods as well as a preservative in cheeses. It is also a significant precursor in many industrial processes such as pharmaceuticals, plastics, plasticizers, textile and rubber auxiliaries, dye intermediates, as well as flavorings and cosmetics.

* 1. Environmental Review

Safety concerns for the chemicals synthesized and utilized in this process are discussed below:

It is possible to use propionic acid as a bactericide and fungicide because it has been EPA certified to have low toxicity to fish, invertebrates, birds and mammals. Propionic acid is used primarily indoors and used outdoors in small amounts. When used outdoors, propionic acid was metabolized by organisms into harmless components and has thus been deemed not harmful to the environment. Propionic acid is non-mutagenic and has overall been observed to not be harmful. Contact with concentrated solutions of propionic acid however, may cause damage to eye and bodily membranes as the solution is corrosive. Protective clothing should be used when handling the compound in its purer forms.

Propionaldehyde is the intermediate product produced in the two step reaction and while it is only available in small amounts in the final product it is still necessary to know as much about this as possible. Propionaldehyde, according to the EPA, is not a carcinogen, nor does it have any reproductive effects on humans. Chronic effects: adverse effects on the body with symptoms that develop slowly due to prolonged exposure to something harmful and do not subside once the exposure is no more, are not associated with exposure to propionaldehyde. Acute affects on the other hand, adverse effects that subside once exposure is terminated, results have proved to be inconclusive in humans though animals have shown moderate to acute toxicity to the substance.

Ethane is the side product of the first reaction and does travel through the process in small quantities, therefore knowing the safety issues regarding this chemical is imperative. According to OSHA, ethane is an asphyxiant which means that it will displace oxygen and lead to suffocation in sufficient quantities. Also it is explosive as such should be kept from hot surfaces and areas to avoid ignition.

Rhodium is a very rare platinum group element. It is combustible in dust when in the powder form. Rhodium is quite toxic if inhaled, though this will not be a problem as the Rhodium based catalyst will be used on graphite supports and immobilized in a packed bed. It is also a skin irritant, fortunately as it is immobilized in a packed bed, there will be very little handling of the catalyst. When disposing of the catalyst, very strict disposal regulations must be followed: Currently Rhodium not classified as harmful to the environment, however this is due more to a lack of information than it is a standard based on test results and observation. Over time environmental regulations may come into being which will affect the method of disposal for this plant’s first catalyst.

A cobalt catalyst is used in the oxidation of propionaldehyde to propionic acid. Cobalt (II) iodide generally has a low toxicity; however, there are acute and chronic effects when exposed to larger amounts of cobalt iodide. Acute effects include: shortness of breath, systemic effects, skin irritation, eye irritation, and cornea damage. Chronic effects include: respiratory sensitivity, nodular fibrosis, thyroid disease, pimples, boils, black and blue spots, hives, and blisters. The probability of these effects occurring is minimal as contact with the chemical is extremely limited and controlled. To control the exposure of the cobalt to the operator, a containment box will be utilized so to avoid any health effects. Operation of Cobalt Iodide will not be performed without safety clothing and a breathing apparatus.

Of the two feeds, syngas is the one that can cause the most problems if there were to be a leak in the piping. The components of the syngas being fed into the plant as mentioned previously are hydrogen and carbon monoxide gas. These components are of course hazardous to humans, the monoxide can be inhaled and cause carbon monoxide poisoning, while the hydrogen gas can easily ignite and cause a major explosion. To assure a safe environment for the employees the piping carrying the syngas will be reinforced and inspected regularly. Also the initial reaction involving the syngas takes place in a bunker so as to contain any explosion that might possibly occur.

Ethylene like ethane is an asphyxiant and can potentially suffocate anyone who breathes in the gas. To prevent this from happening all workers will be required to have masks on while on the process floor. Ethylene, also like ethane, is a threat to combust and cause a major explosion so the pipes will be placed away from anything which can increase the temperature of the feed past the ignition point.

All pipes carrying large amounts of combustible compounds must be inspected regularly in order to ensure there are no leaks.

* 1. Specifications to Meet Industry Standards

The industry standard for propionic acid is currently to have 99.5 wt% purity. In order to achieve this goal the product will be separated many times throughout the process before the reaching having the solution concentrated and separated in series in order to remove the cobalt and purify the product. This basis was not met as the propionic acid leaving the process has a purity of 99.3%.

* 1. Clear Statement of Feedstock

The feedstock to be used in this process is synthesis gas made by Team Foxtrot and Ethylene obtained from Lyondellbasell. The synthesis gas or syngas will be created from coal obtained from Illinois coal basin number 6 in southern Illinois. Because coal is being used as a source for syngas, the coal will have to be heavily treated in order to have it meet the specifications of the process. Multiple processes take place in the purification of syngas in order to obtain a 1:1 mole ratio of CO to H2 which is the ratio necessary for the synthesis of propionaldehyde. The syngas will be received at the conditions of 300 psi and 250 °F. The amount of impurities in the syngas is not a problem as the Rhodium catalyst is extremely durable and able to tolerate many poisons, although team foxtrot has been instructed to have little sulfur in the syngas.

The other feedstock for the synthesis of propionaldehyde is ethylene. It will be obtained by pipeline at industrial standard purity of 95 wt%. It will be obtained at 420 psig and 70 °F which is near the conditions of the reaction.

Oxygen will be fed into the second reaction which is the oxidation of propionaldehyde to propionic acid. Oxygen will be obtained from the air around and thus is assumed to be at ambient conditions. As mentioned before, as air is being fed in, it will enter a membrane separator which will create a gaseous mixture of 85% oxygen and 15% nitrogen gas, which will then be used for the oxidation. The nitrogen component is not known to react with any species in solution and as such will not hinder the reaction at all.

Also the cobalt (II) iodide will need to be dissolved into water which does not contain either potassium or carbonate ions, as potassium carbonate is the only know poison for the cobalt catalyst.

* 1. Recovery Systems

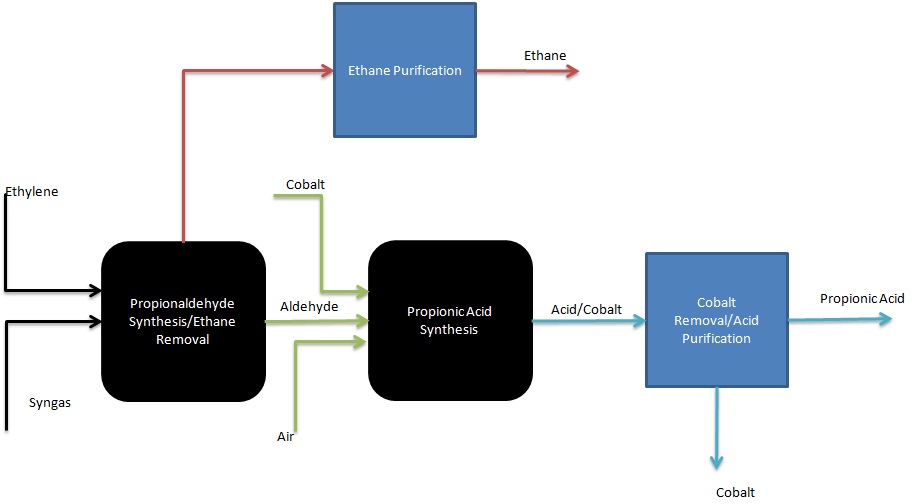
Exit of 1st reactor – unreacted hydrogen and carbon monoxide

Cobalt catalyst exiting the 2nd reactor 🡪 is then precipitated out and filtered and recycled

Ordinary steel is unsuitable for the handling of propionic acid. Aluminum is only resistant at room temperature and to anhydrous, concentrated propionic acid; at higher temperature corrosiveness toward aluminum varies with the concentration of acid. Thus the corrosion maximum for 50 oC lies at 75% acid, whereas there are two maxima at the boiling point, a weaker one at 1% and a strong one at 99.8% acid. Copper and copper alloys are stable toward propionic acid up to its boiling point, but only if the solutions are free from air or oxidizing substances. Of the stainless steels, the ferritic chromium steels (13 – 17% Cr) are unsuitable because propionic acid tends to cause pitting. Generally, austenitic CrNi steels and CrNiMo steels are used for handling propionic acid. However, impurities in propionic acid can make the use of titanium or Hastelloy (e.g., Hastelloy C-22) equipment necessary, even below the boiling point. Above the boiling point, up to about 230 oC Hastelloy C-22 has shown excellent resistance even under oxidizing and reducing conditions. Above 230 oC only silver has proved to be a suitable material.

Containers made of aluminum with a purity of 99.5% or alloyed steels are suitable for storing pure propionic acid. Aluminum is unstable toward aqueous propionic acid. Polyethylene containers can be used for temporary storage of propionic acid and as small packing drums. Plastics are not recommended for long-term storage. Glass-reinforced plastics are unsuitable even for short-term storage. HASTELLOY® C-22® alloy - Used to store the corrosive propionic acid, even at high temperatures.

1. **Block Flow Diagram**

Figure II.1: Block Flow diagram

In figure II.1, a generic version of the process is shown in order to glean a sense of what is happening in the process before looking at the more detailed flowsheet and process flow diagram.

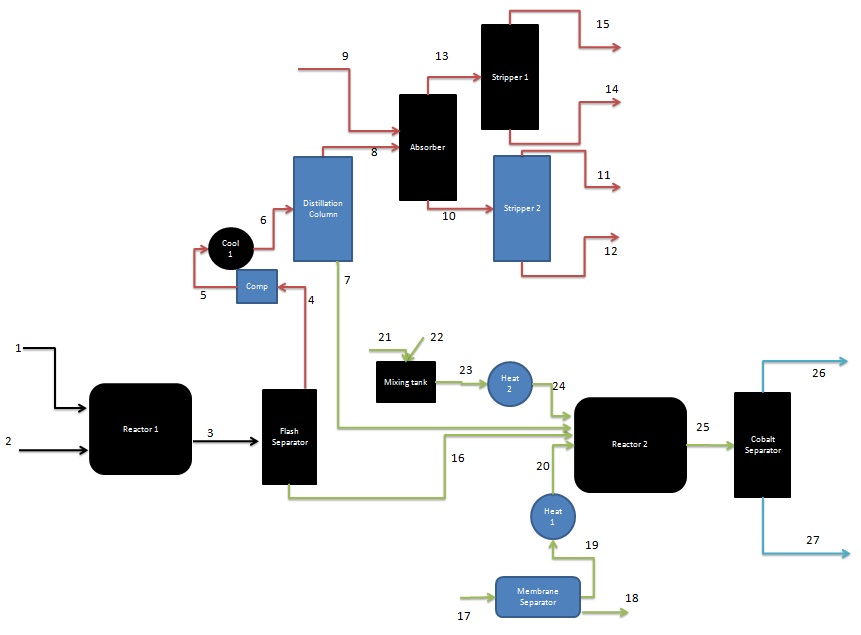


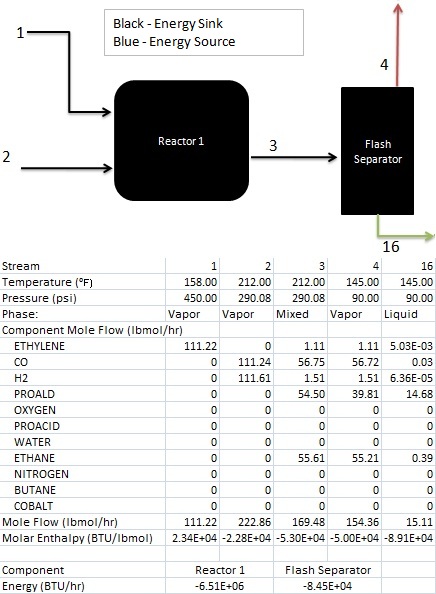
Figure II.2: Overall flowsheet of process

The above figure is an overall view of the process in which syngas will be transformed into Propionic acid. Ethylene and syngas will be reacted at 212 ºF and 290 psi using a rhodium catalyst to produce a Propionaldehyde intermediate product. Unfortunately, for the rhodium catalyst there is a 50% selectivity towards ethane thus hindering the production of Propionic acid. The ethane will be separated from the unreacted reactants, the Propionaldehyde will be sent onward to the second reactor and will be reacted with oxygen using a cobalt catalyst in order to form Propionic acid. For a more detailed view of the process with stream summary please see appendix IV. Materials and Energy Balances.

1. **Process Flow Diagram**

See conceptual control scheme, Appendix IX.

1. **Material and Energy Balances**

Figure IV.1: Summary of reaction

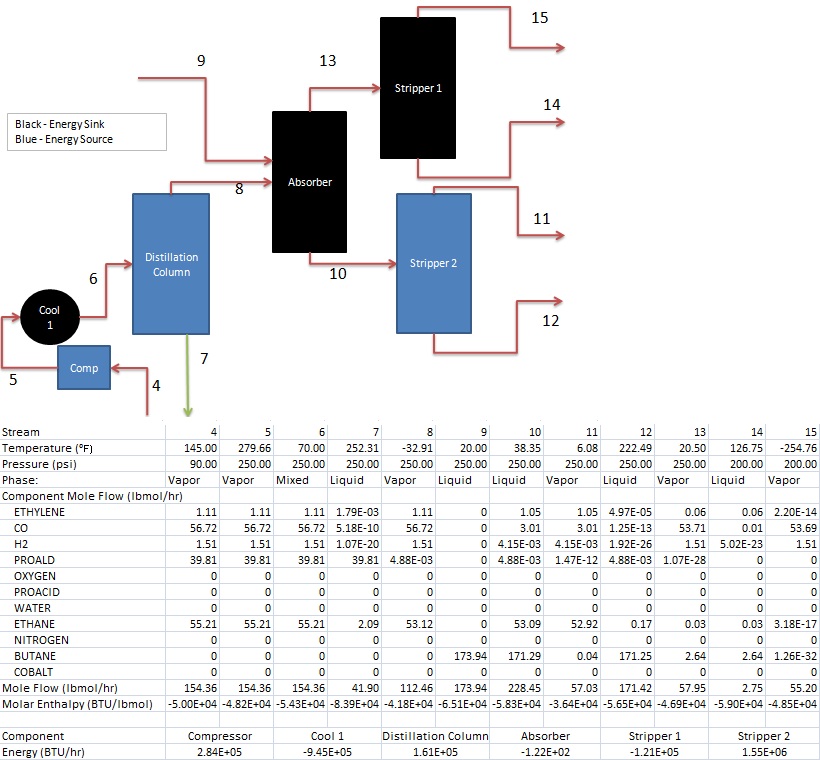


Figure IV. 2: Recovery of Ethylene

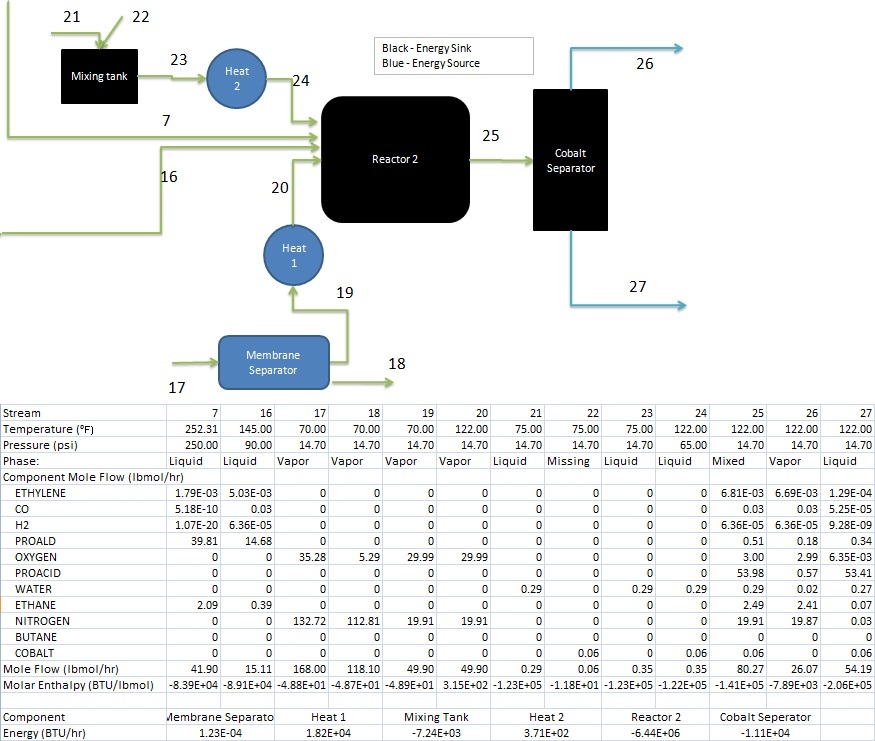


Figure IV. 3: Oxidation of Propionaldehyde

1. **Calculations**

Stripping Column Material balance (Streams: 13,14,15)

57.94534 lbmol/hr = (2.745341 + 55.2) lbmol/hr

Energy Balance (Used in Appendix IV):

Across each block:

Energy Balance to find flowrate of cooling water

1. **Annotated Equipment list**

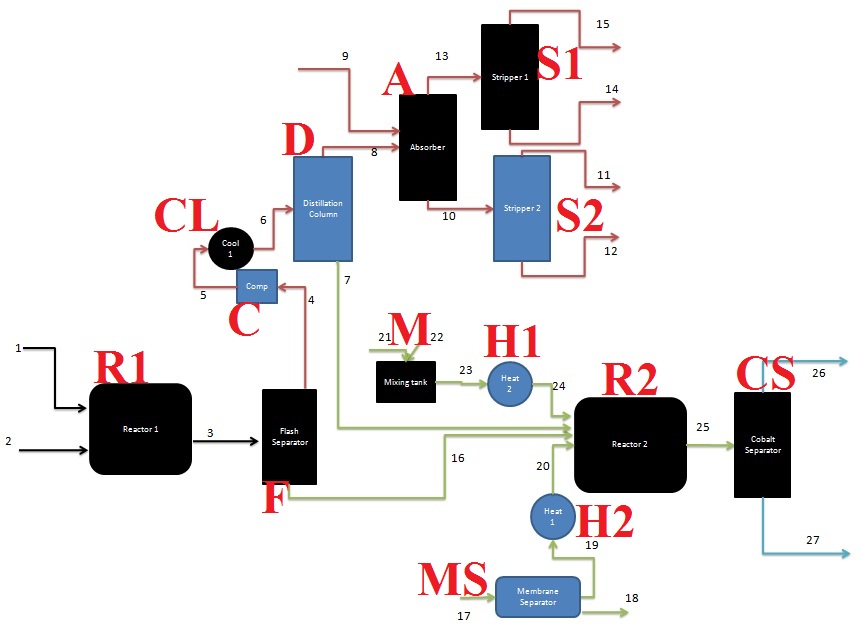
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Figure VI.1 Labeled Components of System

The above figure VI.1 depicts each component in the process tagged with a component ID in order to lessen the confusion with pieces of equipment that are utilized more than more.

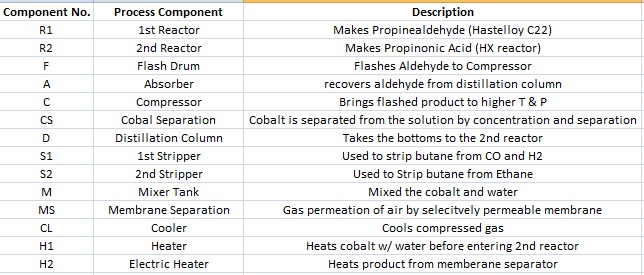
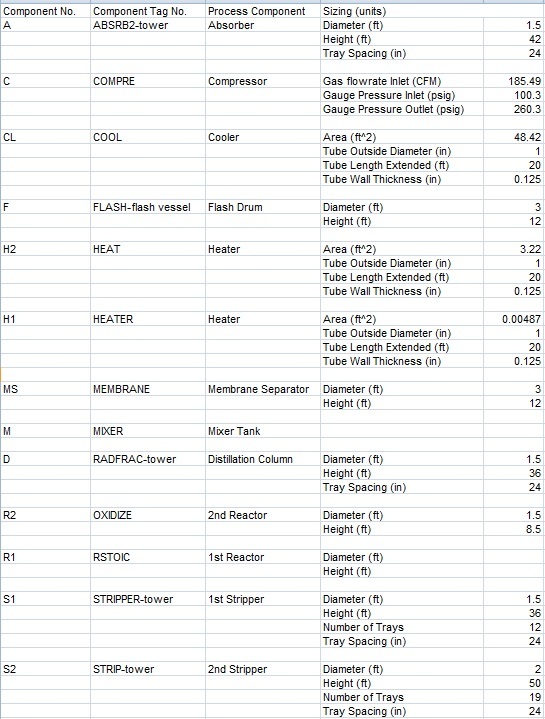


Figure VI.2: List of component pieces



The information from the above chart comes from an Aspen Plus simulation which was sent to Aspen Icarus Process economic analyzer to determine sizing and costing of individual pieces of equipment.

1. **Economic Evaluation factored from equipment cost**

At full production, if 33000 ton/year were produced, the net present value and IRR were quite favorable at $212 million and 38% respectively. The process, unfortunately, produces 16000 tons/year of Propionic acid and thus the economics are much less favorable at this production rate. The actual NPV and IRR are -$20 million and 4% which is an extreme change from running the process at full production.

The capital cost of the process has been estimated to be $57.8 million with a yearly recurring operating cost of $28.6 million. With the project grossing $28.8 million per year, with Propionic acid prices at $1800 /ton the estimated break-even point was 18.5 years. Having a process with such a long break-even point is inadvisable as the numbers from the economic evaluation are projections into the future of what may happen and not what will. Because of this, 18 years is a long time to wait to have the process pay for itself as the fluctuations in the industry and the market could put the operation out of business before a profit has been made.   
 Because the economics that have been done are merely projections of what might happen in the future it becomes necessary to determine the how sensitive the profitability is to the with economics variables. The economic variables that were analyzed for profitability sensitivity are capital cost, price of syngas and price of Propionic acid as shown in the following graphs.

VII.1 Sensitivity analysis over Capital cost

The sensitivity of the capital cost shows the process the profitability of the process is very much affected by the capital cost of the process. The wider range of IRR over the range of the capital cost shows that the profitability is sensitive to the capital cost. Efforts were made to keep the capital cost down in order to maximize profitability.

Graph VII.2: Sensitivity analysis of syngas

The profitability is also quite sensitive to the amount that will be paid to team foxtrot for syngas. If team echo were to pay more money to foxtrot it would not be long before echo would reach a negative profit value. The profitability for team echo is so low at 16,000 ton/year of Propionic acid that it is very difficult to find an economic variable that does not greatly affect their profitability.

Graph VII.3 Sensitivity analysis of Propionic acid price

Product price will always be an object of major sensitivity. Price of product is the income of the plant thus it is highly unlikely that there exists a plant that us not sensitive to the price of its products. While the graph shows that team echo should sell their Propionic acid at a higher cost that would not be economically feasible as it would exceeds the current bounds of the market price of Propionic acid.

1. **Utilities (fill in table)**

|  |  |  |
| --- | --- | --- |
| **Component using Steam at** | **Component ID** | **Flowrate:** (#/hr) |
| Stripping Column | S2 | 1845 |
| Stripping Column | S1 | 85 |
| Distillation Column | D | 333 |
| Heat Exchanger | H2 | 20 |
| Heat Exchanger | H1 | 0.27 |

|  |  |  |
| --- | --- | --- |
| **Component using Cooling water** | **Component ID** | **Flowrate:** (#/hr) |
| Reactor 1 | R1 | 152877 |
| Reactor 2 | R2 | 25853 |
|  |  |  |

|  |  |  |
| --- | --- | --- |
| **Component using Refrigerant** | **Component ID** | **Flowrate:** (#/hr) |
| Heat Exchanger | CL | 4864 |
| Distillation Column | D | 2529 |
|  |  |  |

1. **Conceptual control Scheme**

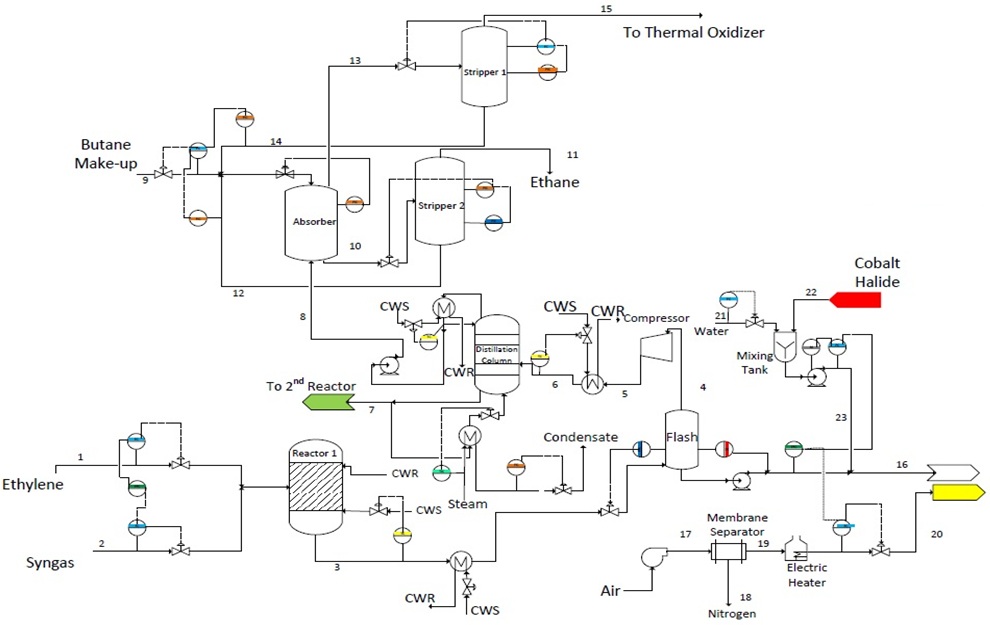


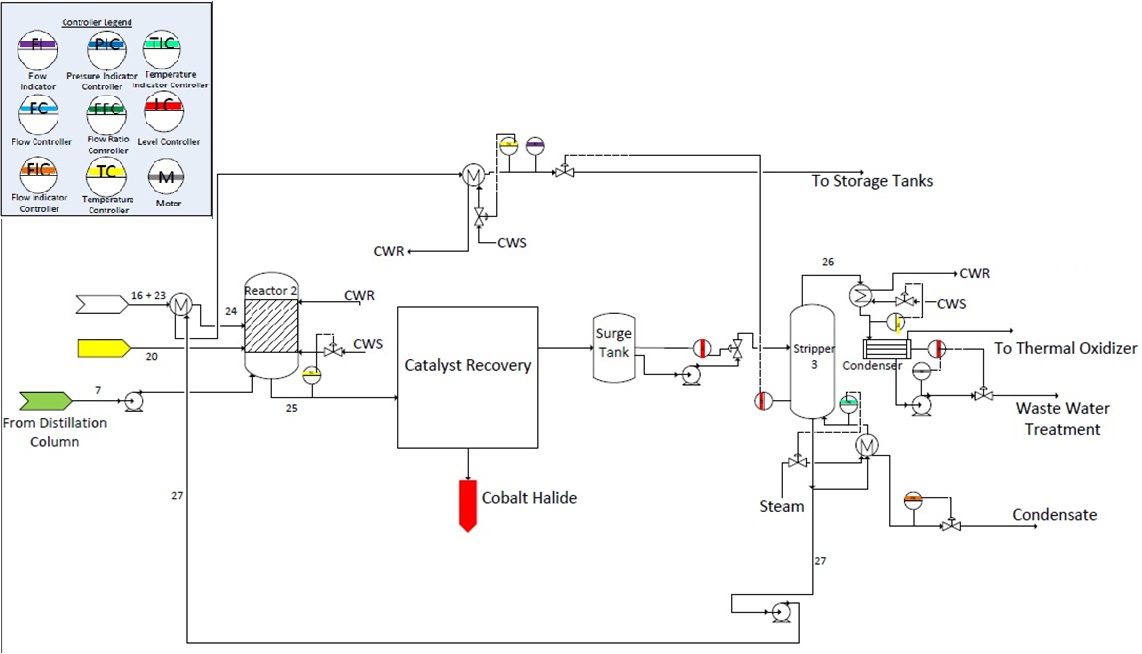
Figure IX.1: Process flow diagram part 1****

Figure IX.2: Process Flow Diagram part 2

1. **General Arrangement (Plant Layout)**



Figure X.1: Pictorial image of Plant land

Shown in the above figure is a screen shot taken from google earth of the plot of land in Morris, Il 60450 that will be used by teams echo and foxtrot to build their plants. The distances shown in the figure were measured using google earth as well. Care was taken to ensure that ample transports into and out of both facilities was available. Care was also taken to ensure that the plants were a reasonable distance from any communities in the area.

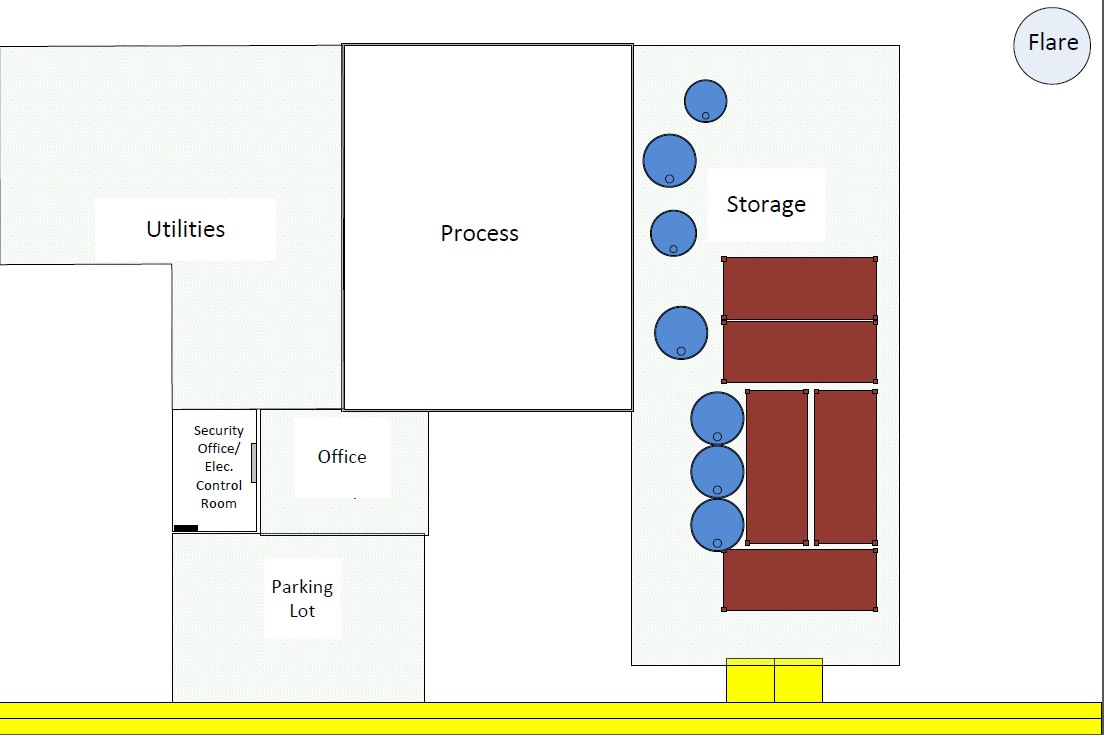


Figure X.2: Schematic drawing of plant layout

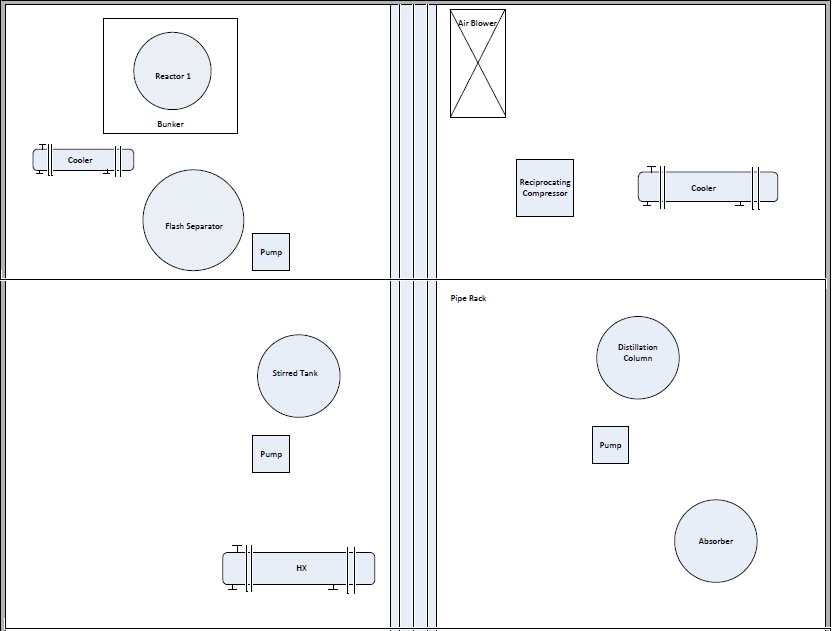


Figure X.3: Top half of floor plan

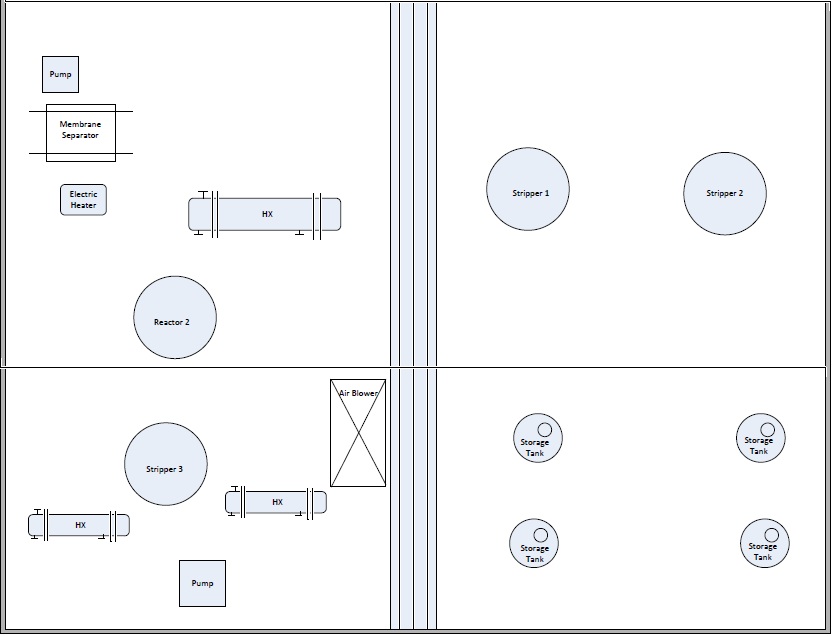


Figure X.4: Bottom half of floor plan

1. **Distribution and End- Use Issues review**

Propionic acid was selected to be produced due to its wide range of uses. Uses of Propionic acid include: Mold inhibitor for various animal feed, food preservatives, pharmaceuticals, plastics, plasticizers, textile and rubber auxiliaries, dye intermediates, flavorants and cosmetics.

Propionic acid in the food preservative industry is the aim of this project. Not only do fast foods use Propionic acid in their food preservatives but grocery stores also utilize Propionic acid to increase the shelf life of food. With this the demand for food will never waver as people will always need to eat regardless of the economic atmosphere.

Use of Propionic acid in plastics was also seriously considered as the main focal point for selling of the final product. While plastics are common in daily life and always in use, it was decided that the food market would be more stable and to primarily target, and to secondarily target the other uses of Propionic acid.

1. **Constraints Review**
2. Feedstock Definition

Synthesis gas or syngas is a gaseous mixture primarily comprised of carbon monoxide and hydrogen. The syngas that will be utilized by Team Echo will be created from coal obtained from Illinois Coal Basin number 6. Because the syngas is coming from coal, desulfurization will need to take place as sulfur can poison the catalysts. CO2 sequestion will also take place in order to have a greater purity of syngas. Coal is an abundant resource and is currently the second greatest provider of energy, coming in second only to petroleum. This coupled with projections that coal will indeed be around for at least the next two hundred years leaves hope that obtaining the necessary coal for synthesis gas will not be a problem.

Ethylene is the other portion of feedstock utilized in the synthesis of propionaldehyde. Ethylene is currently being produced and sold at large quantities at Lyondellbasell in Morris, IL. For this reason, as is discussed in Location Sensitivity Analysis, both Team Echo and Foxtrot have decided to be located in Morris. Due to the adjacent plant location to the ethylene supplier, transportation issues for this particular feed has been eliminated. As for the production of ethylene, it is an abundant hydrocarbon that is easily synthesized and hopefully will not be an issue in availability.

1. Conversion Technology Description

Both of our reactors will be compressed heat exchanger reactors, obtained from Chart Energy and Chemicals Inc. This specific type of reactor allows for the reaction of gas phase as well as liquid phase feeds and the immediate removal of heat from the system. The first reactor will be made of stainless steel while the second will be made of hastelloy. Both reactions that take place in this process to synthesize propionic acid (synthesis of propionaldehyde followed by the oxidation of the aldehyde) are highly exothermic and will require a medium to absorb all that heat in efforts to reduce the cost of energy for the plant as a whole. This specific type of reactor allows for the immediate absorption of exothermic heat which can then be used to increase the temperature for streams later in the process. The synthesis of the aldehyde intermediate takes place under the influence of a rhodium based catalyst which will be on a solid support, to account for this, Chart Energy and Chemicals creates a specific type of the compressed heat exchanger reactor with room to place packing materials inside the open channels of the reactor.

The standard compressed heat exchanger, without room for packing materials, will be used for the oxidation of propionaldehyde as the catalyst for this reaction is a dissolved cobalt salt.

1. Separation Technology Description

There are multiple methods of separation in this process such as distillation columns, flash separators, and precipitation.

After the first reactor there is a flash drum that will be used to separate some of the Propionaldehyde from ethane and unreacted reactants. They will be flashed to 90 psi and 145 °F. The Propionaldehyde is sent onward to the second reactor in which it will be oxidized into Propionic acid.

The by-product ethane will be removed from the system by using an absorption and two stripping columns. The vaporous product from the flash in the preceding paragraph will be sent into an absorbing column and the ethane will be absorbed into butane which will be fed into at the bottom and top of the column respectively. The ethane-butane stream will exit the bottom of the absorption column and sent into a stripping column. The unreacted reactants will exit at the top of the absorbing column and sent into a stripping column in order to recover any butane that may have exited in the top of the column.

The ethane-butane mixture from the preceding paragraph will be sent into a 15 stage stripping column at stage 7 in order to purify the ethane to be sold, as well as to recover the butane in order to reuse it. The rest of the butane will be recovered from the unreacted reactants by utilizing another 10 stage stripping column. The feed to this stripping column will be fed in at stage 5. 2 moles of butane will still be lost with the ethane stream and thus a make up stream of butane entering the absorber becomes necessary.

Oxygen is separated from air by membrane separation. It was assumed that there would be an 85% recovery of oxygen in the permeate stream based upon lab experiments performed in the Unit operations laboratory class. Air will be taken in and used for the oxygen source. The retentate stream is purged from the system.

Cobalt is crystallized out of the solution by concentrating and separated. After catalyst recovery the propionic acid-water solution is sent to a distillation column. Water exits the top of the column. Propionic acid exits the bottom of the column, is cooled and sent to storage.

1. Production Description

The end product of this process will be a 99.3 wt% propionic acid, which is slightly lower than the industrial purity level of 99.5 wt%. Propionic acid is a colorless liquid which gives off a pungent odor; chemically it is a three carbon chain carboxylic acid which has a similar density to water at ambient conditions also this compound is miscible in water much like other short chain organic acids.

1. Location Sensitivity Analysis

It has been determined that teams echo and foxtrot will be located next to each other. That being said, the two feedstocks in which echo would have any problems obtaining are syngas and ethylene. As the syngas team will be located next to echo, then ethylene becomes the determining factor in location for team echo.

Based upon this there were two locations which initially piqued team echo’s interest based upon large production rates of ethylene. Upon research it was determined that Texas and Louisiana were viable choices because of large ethylene production. This was later ruled out and Morris was selected upon the completion team foxtrots material balance around Illinois coal basin number 6.

1. ESH Law Compliance

According to the EPA both propionic acid and propionaldehyde have been classified as non carcinogenic. OSHA classified propionic acid as a non air contaminant.

Ethane and ethylene are both asphyxiants and as such must be contained, especially because the plant location is adjacent to a residential area.

Both catalysts are toxic and must be disposed of properly. This does not mean flushing them down a drain as both are harmful to the environment. Both the rhodium catalyst and the cobalt salt must be disposed of as hazardous chemicals.

1. Turndown Ratio

The turndown ratio for this process is set at 50%, the reason it is set at this value is to avoid any weeping in the distillation column trays and also to avoid the pipes of the heat exchangers from cruding up. With half the flow rate, it should be enough to have enough flow to keep all of the components of this process in working order without any substantial and expensive buildups or backwash.

1. **Applicable Standards**

The Aspen simulations used were able to thermally rate all of the heat exchangers, but provided little to no help in designing them. To help design heat exchangers for our applications to withstand our operating temperatures and to meet our mechanical and thermal criteria we looked to TEMA – Tubular Exchanger Manufacturers Associations –for further information.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Utility | Typical TEMA type heat exchanger | Description of TEMA type heat exchanger | Removable tube bundle | Tubes can be cleaned internally by rodding | Non-hazardous liquids and gases below 40 barg (~580 psig) | | Non-hazardous liquids and gases above 40 barg (~580 psig) | Hazardous liquids and gases | No gaskets in contact with process side | Ability to resist thermal shock |
| Below 190°C | Above 190°C |
| Majority of Heat Exchangers | AEW  BEW | Externally sealed Floating tube sheet | Yes | Yes | Yes | No | No | No | No | No |
| Heat Exchanger Involving Cobalt Catalyst | AEL  BEM | Fixed tube sheet | No | Yes | Yes1 | Yes1 | Yes | Yes | Yes2 | No |
| \*Note: !. Expansion bellows may be required 2. Shell side only | | | | | | | | | | |

For all but one of the heat exchangers there will not be any hazardous liquids or gases. As a result, these heat exchanges follow a certain type of arrangement. According to TEMA, these externally sealed floating tube sheet heat exchanges follow one of two arrangements – these being an AEW or BEW arrangement. For the one heat exchanger that involves a hazardous liquid – containing our cobalt catalyst – the more basic heat exchanger that TEMA offers capable of containing hazardous liquids was chosen. This fixed tube sheet heat exchanger comes in one of two arrangements – either an AEL or BEM design. From these three-letter coding system a picture can be built up of the final shell and tube assembly, consisting of a front-end stationary head, a shell type, and a rear-end head. For most of our heat exchangers, their design will look one of two ways:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Three-Letter Coding System | Front End Stationary Head Type | Shell Types | Rear End Head Types |
| Majority of Heat Exchangers | AEW | A | E | W |
| BEW | B | E | W |
| Heat Exchanger Containing Cobalt Catalyst | AEL | A | E | L |
| BEM | B | E | M |

1. **Project Communications File**

**Wednesday Conference Meeting 03/30/11**

* Working on plant layout (using google 3-D)
  + google sketchUp
  + can use plot plan 2-D...no need for 3-D
  + also using Visio
* Working on finishing up economics
* PFD is in Visio format
  + post screenshot to make it seen for all

**Tuesday Conference Meeting 03/15/11**

* What is important for process to operate properly
* Need schematic of necessary controls in place
* ISA symbology
* Distillation column- temp, composition, temp change, over head receiver, not dry pump, must have some level in the bottom of the columns, platform wert twenty or thirty feet, platform with ladder
* Hx- must be able to pull tubes, need space for this, orient hot dog style,
* control room, locker room, storage tanks, all equipment must be located, must have access space between equipment

**Notes taken during Meeting 3**

Engineering challenges Use block flow in presentation In Econ, total cost total profit, not all components Spec on period of investment Cost of money that every group will use Interest cost of money Every group will be using the same assumptions Removing gas, there is am adsorption and stripping process Hotel used engineering world for costs or sizing? Must remember to number slides Paired groups do economics together Look into what to do with waste, thermal oxidizer? Adiabatic flash to size heater

**Wednesday 03/09/11 Telecom Meeting**

1. Presented more info than expected, good!
2. Next week, March 14-18, 2011: need to meet with Shannon possibly Tuesday but she’ll email us

So that we can work on:

* + 1. Finalizing PFD
    2. Finalizing Material balance
    3. Preparing proper layout of process
    4. And sizing

1. Need to know flash conditions
2. The new reactor conditions for 1st and 2nd reactors need to be defined
   1. If there’s a temperature rise, state
   2. Address how to get heat out of there
3. Crystallization: it’s a point below saturation
4. there was water in 2nd reaction but need to state
5. search more on cobalt iodide
   1. price
   2. solubility in water, propionaldehyde and propionic acid

**Tuesday 03/08/11 Questions and suggestions made by Mentors:**

Presentation questions:

* sizing of the distillation column are usually ~85 ft for a 35 theoretical stages
* Aldehyde: vapor & flashed
* HX between reactor & flash?
* Streams 4 & 7 should be same temperature
* Bubbling gas through tank, spark O2 to it
* Separation of propionic acid from water, how soluable is it in water?
* Are we crystallizing or precipitation it out of the process?
* Put water on Co catalyst…it will need water make-up stream

**Wednesday 02/23/11 Telecom Meeting**

* We need more details especially on economics in order to increase grade on presentation
* We have more info on nickel carbonyl and it shows up in ASPEN as a gas phase only which is causing a problem because literature says it’s been in liquid form
* Method of recovering our catalyst (cobalt halide)? We’re getting high reflux ratio
* Ask Prof. Nitche on ASPEN
* CSTR deals with liquids but our design is not a CSTR, can use for place holder, think about using PFR…
* Use dielstein…orgo synthesis
* Look at patents for using catalysts
* Post correction on Wiki of specs
* What manufacturers use our catalyst?
* If it’s only one stream we’ll have to keep buying new, if we know price and what we need, we can get by with this
* Use ASPEN for equipment sizing but not all of them
* We need details on one of the operations in terms of sizing, looking at one area and making sure we have everything we need, look at it more closely and make sure everything is checked
* Energy sinks, look at where energy is coming from and into deltaH across a reactor
* We will have to see the design and sizing of reactor which ASPEN does not recognize

**Thursday 02/17/11 Telecom Meeting**

* Write abstract by Monday 02/21 as it is due then
* 5-6 page progress summary is due on midterm day, week 8
* Email CoX manufacturers to get conversion rates and other important information
* Integrate catalyst into Aspen
* Look into catalyst interaction and recovery
* MSDS sheets for more safety information
* Fix economics, no more place holders
* Use knovel in research
* Divide utilities cost with Foxtrot
* Reactor information, CSTR implies liquid
* Pumps compress liquids and Compressors compress gasses
* Find out about Drew’s catalyst
* Prove that separation is occurring in all separators
* Heat of compression
* Reciprocating compressors don’t go above 250 °F use multistage

**Tuesday 02/15/11 Questions and suggestions made by Mentors:**

* Note the sources of the info and numbers brought up
* Note the $/yr or day or month that are being calculated in the pricing and economics
* Use scientific notation, commas, an overall number to describe an estimate without many and ongoing significant figures
* Price of syngas is high...get a better estimate
* Estimated capital cost is very low, get a better estimate
* There are equipment/steps needed in the process such as: decanter, recycle, to recover catalyst on regular basis
* something to make sure catalyst doesn't go anywhere wrong
* heat removal step
* where to flash out product
* CSTR is a design reactor or are we modeling it like that in aspen?
* show what it is/what it's like
* How do we get aldehyde out of liquid?
* stick with outline as placed in beginning of presentation
* include capital cost in a safety system
* place process overview with total #s in and out, this can be displayed in a diagram
* improvise the block flow diagram to show what's in the streams and display numbers

**Meeting with our mentor**

* Do we need refrigerant at recycle stream? When reaction is happening at high temperature. Show her price of refrigerant and if ok to use.
  + Depending on where we are letting out to…not necessary
* How much refrigerant/cooling water we need?
  + How much heat is generated should tell us how much cooling water we need
* How much catalyst we need? How to find that?
* How long for 1st and 2nd…may not need large volume. How long we need to be in, residence time. Ask Dennis/Bill
* Find reactivity and selectivity
  + Do we need cooling tower?
  + Sharing with other grp their cooling tower.
  + Look into air coolers
  + Look into heat effluent exchange
* Cobalt propionate or cobalt halide which to choose?
* How to include catalyst in aspen?
* Have you contacted Adam Kenya about the Sulfur concentration of syngas from foxtrot?
  + She talked to him but Adam will talk to foxtrot so that they find a solution for it.
* Specifics on utility costs? What do we include?
  + Add into the ppt
* Use multiple stage compressors with ethylene
* More hydrocarbons are stored in spheres
* Vapor pressure will be high for ethylene

Things to add to the power point:

* Add a row for temps and pressures for each stream number
* Enthalpy can be found from aspen in the stream summary, use those, they’re fine. If we don’t want to use, address that we don’t and state how we’ll find it.
* Change 30kt/yr to English units
* Fix environmental review=add nickel carbonyl
* Nickel Carbonyl: OSHA has permissible exposure: 0.001ppm for gen industry, threshold limit is 0.05ppm, grp1 human carcinogen.
* Cobalt Iodide: OSHA 0.1 cob/m3 (rate 3-reacts explosively with water)
* Fix block flow diagram update according to aspen-kevin
* Update competing process slide (we are doing 1st rxn but we’re not doing 2nd)
* Fix graphs, sharpen view
* Cheaper to transport coal than ethylene-slide “plant location” fix it
* Interest on loans we’re getting to build…we have negative cash flow initially?
* How long will it take to build the plant?
* Delete 3rd point on slide: estimates
* Slide: catalyst of nickel carbonyl change unit to English
* Plant Standards EPA, ASME (for pipe standards), OSHA, and FDA: find out product purities, to be generally recognized as a safe list,
* Price graph: need a current date
* MB in hand calc
* Catalyst life? Nickel bought every yr but cobalt, include the cost as an initial cost as well as annual
* Selectivity of catalyst?
* Recovery of catalyst? Flash, not sure if we’re getting 100%
* We r reacting in gas phase in 1st reactor

**Thursday, February 10, 2011, Conference call**

* what we are working on:
* Material and Energy Balances
* Aspen flowsheet
* Aspen Material Balance
* Hand calculations
* Economics
* pricing on catalysts
* Cobalt (II) Iodide
* Nickel Carbonyl
* Utility costs
* Plant Economics
* List of things to look over again:
* Flow sheet with flag streams
* MB & EB around multiple pieces of equipment in a table
* State how this process is going to close
* Need units from lb/yr to lb/hr
* Pay attention to significant figures
* State the hrs/yr the plant will run
* Number all streams on flow sheet
* Look further into:
* What is the syngas coming out at (T & P)?
* Run Economic Analysis
* Size compressors with knowing what's coming in
* Multiple stages for compressor

**Thursday February 3, 2011, Conference call**

* What we are working on:
  + economic evaluation
  + carbon or stainless steel?
  + over 800 F cant use carbon
  + material and energy balance
  + have an in-progress aspen flowsheet for material balances
  + will start on energy balances soon
* Location: Morris, Il
  + make sure its close to a railroad so its easy for foxtrot to transport coal.
  + Send flowsheet to Shannon when done
* Next conference call: Thursday, February 10th at 1:00 pm
* Discuss time for in person meeting with Shannon
* On the table:
  + Get to Shannon's work after senior design
  + Friday evenings after 4

**Friday January 28, 2011**

Joint Team Meeting: Foxtrot and Echo.

Shannon Brown, Adam Kanyuh

* Purpose of the meeting:
  + Things seem in "flux"
  + Establish a feed basis (should be given to Team Foxtrot by Monday)
* What we need to do:
  + Send an email to Foxtrot, Shannon and Adam stating the composition and the feed rate required
  + what contaminants can we ignore?
  + what will poison our catalyst?
  + what exactly are our requirements?
  + Location?? (information needs to be handed over to Foxtrot sometime next week.)
  + ﻿its easier to transfer coal compared to transferring ethylene, so this decision should be made as a joint group.
  + some locations to look into:
  + st. louis (marathon petrochemical plants)
  + do they sell ethylene crackers?
  + gulf coast
  + look up where ethylene crackers are readily available
  + send a few locations to foxtrot so they have a choice as well
  + Utility conditions?
  + Are there any conditions that both the teams need?
  + compare conditions with foxtrot and determine if there is anything we both can use
  + example: steam pressure levels
* What we know:
  + Echo needs syngas to be at these ranges:
  + temp: 250-300 C
  + pressure: 100-300 bar
  + Echo is using nickel carbonyl and cobalt as catalysts
  + Foxtrot currently want their gassifier to be located in Illinois # 6 Basin/Butiminous
  + located in southern illinois

**Notes from first meeting with Shannon (Jan 23, 2011) meeting:**

* Spec of impurities to gasifier team
* How pure is the feed stock?
* What would poison the catalyst
* Produce 80 kilotonne/year? Share of world market?
* Outline of what we are covering – week by week
* On powerpoint
* Look at schedule
* Focus of the week
* Economic analysis of buying vs. making ethylene
* Add quantity to design basis
* Check up solid support for catalyst
* Autoclave? Does it dissolve better?
* Acyl rhodium tetra carbonyl
* Lowers temp to 45 C
* Ceramic catalyst- talk to Meyers
* State of catalyst?
* Rough economics – meeting two
* Set up report on wiki
* More on environment review after catalyst

**Meeting: January 20, 2011**

Working Title: Synthesis of Plastics from Propionic Acid

Design Basis: Why we need to produce plastic. (In Discussion)

Plastics being looked at:

* Polyethylene
  + Polyethylene (or polyethene, polythene, PE) is a [family](http://www.ehow.com/relationships-and-family/) of materials categorized according to their density and molecular structure. For example, ultra-high molecular weight polyethylene (UHMWPE) is tough and resistant to chemicals, and it is used to manufacture moving machine parts, bearings, gears, artificial joints and some bulletproof vests. High-density polyethylene (HDPE) is used to make milk jugs, margarine tubs and water pipes. Medium-density polyethylene (MDPE) is used for packaging film, sacks and gas pipes and fittings. Low-density polyethylene (LDPE) is soft and flexible and is used in the manufacture of squeeze bottles, sacks and sheets.
  + Read more: [Uses of Thermoplastics | eHow.com](http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBHf3eN) <http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBHf3eN>
* Teflon
  + Teflon is the brand name given by DuPont Corp. for a polymer called polytetrafluoroethylene (PTFE), which belongs to a class of thermoplastics known as fluoropolymers. It is famous as a coating for non-stick cookware. Being chemically inert, it is used in making containers and pipes that come in contact with reactive chemicals. It is also used as a lubricant to reduce wear from friction between sliding parts, such as gears, bearings and bushings.
* Read more: [Uses of Thermoplastics | eHow.com](http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBarTNg) <http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBarTNg>
* *Leaning towards making propionic acid -> polyethylene*

**Wednesday January 19, 2011 (first meeting as a group)**

* Do some research by second group meeting
* Advantages and Disadvantages of gasses being looked into:
* Propionic acid:
  + Naturally occurring
  + Made from ethylene and carbon monoxide
  + Uses and advantages:
  + Analgesic
  + Intermediate product for thermoplastic
* Formic acid:
  + May cause damage to optic nerves
  + Made from methanol, ammonia sulfuric acid, and carbon monoxide
  + Also made from water and carbon monoxide
  + Cheapest to make?
  + Operating at a high partial pressure
  + Simplest carboxylic acid
* Acetic acid:
  + Global demand: 6.5million tonnes/year
  + Made from carbon monoxide and methanol

1. **Competing Processes**

Industrially, propionic acid is currently produced almost exclusively by three different processes:

1) Carbonylation of ethylene with carbon monoxide and water

2) Oxidation of Propanal

3) Direct oxidation of hydrocarbons

The Koch synthesis has been investigated intensively. As a carbonylation reaction of ethylene in a strongly acidic medium, it is a variant of the Reppe synthesis. However, compared with the latter, it never achieved much industrial significance and was carried out with little success.

Other possible sources of propionic acid, which are not used industrially for economic reasons, are its formation as a byproduct in the high - and low - pressure carbonylation of methanol to give acetic acid (2% formation of propionic acid), the direct reaction of ethylene, carbon monoxide, and water over noble-metal catalysts.

Two-step reactions have been described, in which propionic acid is obtained directly from synthesis gas (20 – 60 bar, 150 – 160 oC, Rh catalysts). With the current availability of ethylene and naphtha these processes are, however, not yet competitive. It is sometimes desirable, to use propionic acid produced by natural methods, particularly for the use of propionic acid in flavors and fragrances. Appropriate microbiological and enzymatic processes have been developed, which are usually based on the anaerobic fermentation of starch or sugars. However, the expensive production of this “natural” propionic acid limits its use to special areas of application.

**Carbonylation of Ethylene (BASF Process) (Our Old Process)**

In the Reppe synthesis ethylene is reacted with carbon monoxide and water in the presence of Ni(CO)4 (Nickel Carbonyl) according to the following process: the reaction takes place at high pressure and is characterized by low raw material costs, high conversion, high yield, and a simple workup. Ethylene and carbon monoxide are compressed and continuously pumped into the high-pressure reactor together with the feed solution. The crude propionic acid formed at 100 – 300 bar and 250 – 320 oC is drawn off at the head of the reactor and cooled in a heat exchanger with production of steam. Part of the cooled reaction product is recycled to the reactor for temperature regulation, the majority of it is allowed to expand and is separated into an off-gas and a crude acid stream. Nickel is recovered from the off-gas and led back into the reactor. The off-gas is incinerated with recovery of heat. The crude acid stream is subsequently dehydrated and worked up by distillation in several following columns. The nickel salts that are formed are recycled into the process. The pure propionic acid is finally obtained by distillation. The product residue is channeled out of the process. Variants of the Reppe and Koch syntheses are possible, where the effect of inorganic salts on the reaction conditions and yield are important factors. Boric acid is reported to accelerate the reaction and hinder the precipitation of catalyst salts.

**Oxidation of Propanal (Our Process)**

The oxidation of propanal is an important route to propionic acid. This route is economically attractive although two steps (production of propanal and subsequent oxidation) are required: (1) Propanal is formed in large quantities as an intermediate in the production of npropanol by hydroformylation of ethylene, and (2) the oxidation takes place in plants in which other aliphatic carboxylic acids (n-butyric and isobutyric acids, n-valeric and isovaleric acids) are also produced. A high utilization of available capacity is therefore guaranteed in both steps.

**Propanal Production**

The production of propanal is carried out by the hydroformylation of ethylene. It is favored because, unlike the case of the higher aldehydes, n/isomixtures cannot be formed. Two syntheses compete: the classical cobalt- catalyzed high-pressure carbonylation at 200 – 280 bar, and 130 – 150 oC, and the rhodium- or iridium- catalyzed low-pressure carbonylation at about 20 bar, and about 100 oC. In the high-pressure synthesis the yield is generally impaired by partial hydrogenation of propanal to give propanol. The isolation of the aldehyde takes place, after removal of cobalt, by distillation of an azeotrope with ca. 98% aldehyde content. In the low-pressure synthesis (Union Carbide), the aldehyde can be distilled directly from the reaction mixture in 99% purity.

**Oxidation**

Propanal is subsequently oxidized under very mild conditions at 40 – 50 oC to propionic acid with high selectivity. In the United States propionic acid is produced by the oxidation of propanal by Union Carbide and Eastman Kodak.

**Direct Oxidation of Hydrocarbons**

A large quantity of propionic acid is obtained by the direct oxidation of hydrocarbons, predominantly naphtha. In this process, which is principally used for acetic acid production, formic acid, propionic acid, and an isomeric mixture of butyric acids are formed as byproducts. Whether this process is considered economic for propionic acid production is principally a question of the market evaluation of the different products. The process has favorable raw material costs, but requires a relatively complex workup of the product mixture. The composition of the acid mixture formed in the oxidation can be affected by the reaction conditions (pressure, temperature), the type of reactor (tubular reactor, column reactor), the raw material (naphtha, liquefied petroleum gas), and by the catalyst. If naphtha is used, the proportion of propionic acid in the mixture is about 10 – 15%. In other cases like with 2- methylpentane as a raw material, the proportion of propionic acid can increase to 31%. The total yield of acids does, however, vary considerably with the starting material. **BP Chemicals Process**

Naphtha is preheated to 170 oC and oxidized with air at 40 – 45 bar in several reactors in series. Again, the heat of reaction is used for steam generation. The cooled discharge from the reactors is separated from the reaction off-gas in a separator. Entrained liquid is recovered from the off-gas and recycled to the reactor; the off-gas is then incinerated. The liquid reactor discharge is separated into an organic phase, which contains unreacted hydrocarbons, and an aqueous phase which contains the product mixture. The unreacted hydrocarbons are recycled to the reactor. The low- and high-boilers are separated from the aqueous phase which then gives the crude acid. From this the C1- to C4-acids are obtained by extractive dehydration followed by fractional distillation. Propionic acid is produced by direct oxidation at BP Chemicals (UK), Hoechst – Celanese (United States), and Daicel (Japan).

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